Biobased products from rubber, jatropha and sunflower oil

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Chapter 3

The influence of storage time on relevant product properties of rubber seed, rubber seed oil and rubber seed oil ethyl esters

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Abstract

The moisture uptake/release versus time profiles for two different batches of rubber seeds, one with an initial water content of 3.1 wt% (PT, obtained drying the seeds at 60 °C for 3 days) and another with a moisture content 10.7 wt% (NPT, as received) were determined at 27 °C and a relative humidity of 67% for a period of two months. The moisture versus time curves were modelled using an analytical solution of the instationary diffusion equation and allowed determination of the diffusion coefficient of water in the rubber seeds at 27 °C. In addition, the oil content of the seeds and the acid value of isolated rubber seed oil were also determined periodically for a two months period. The acid value of the isolated rubber seed oil increased from both cases (NPT from 0.84 to 4.19 mg KOH/g and PT from 0.51 to 2.13 mg KOH/g). The effect of storage time and conditions (27 °C, closed container) on the acidity of the rubber seed oil and rubber seed ethyl esters were also evaluated. Freshly isolated rubber seed oil and rubber seed ethyl esters derived thereof have a relatively low acid value of 0.52 and 0.32 mg KOH/g respectively. The acid value of rubber seed oil only slightly increased during storage (0.52 to 0.60 mg KOH/g), whereas the acid value of the rubber seed ethyl esters (0.32 to 0.33 mg KOH/g) is about constant.

Keywords
Rubber seeds, rubber seed oil, rubber seed ethyl ester, storage, acid value

3.1 Introduction

Biodiesel is an important renewable transportation fuel produced from triglycerides like virgin plant oils and waste cooking oils [1-3]. It is commercially available and widely used in many countries such as the US, Indonesia, Brazil, Germany and other European countries. Global biodiesel production grew at an average annual rate of 17 % from 2007 to 2012 [4]. In the US, the biodiesel industry recorded a total volume of nearly 5.67 million ton in 2013, which exceeds the 2.52 million ton/annum target set by the Environmental Prtection Agency's Renewable Fuel Standard [5]. The production of biodiesel in Europe has also increased dramatically in the period 2000-2011 and accounts for 41% of the global biodiesel output [4]. This increase is driven by the European Union objective of a 10% biofuel share in the transportation sector by 2020 [6].

A wide range of oil-bearing crops have been identified as potential sources for the production of biodiesel. Edible oils such as rapeseed, sunflower oil, palm oil and soybean oil account for more than 95% of the current feeds used for biodiesel production [2]. However, there are many concerns regarding the use of such plant oils for non-food applications like biodiesel production and this stimulated the search for alternative feeds for the biodiesel industry.

A possible solution is the use of non-edible oils with a high productivity (oil yield per ha per year). Various studies have been performed to investigate the potential of such oils as the feedstock to produce biodiesel, examples are jatropha, karanja and rubber seed oil [7-9]. The latter oil (RSO), derived from rubber seeds, is considered a promising source because the seeds are reported to contain a high amount of oil (40-50 wt%) [10, 11] and the seeds are currently regarded as a waste. The productivity of rubber seeds is reported to be in the range of 100-1200 kg/ha/y [12, 13]. From a biorefinery perspective, the valorisation of rubber seeds by biodiesel production is highly relevant as it increases the economic attractiveness of the rubber plantations.

The conversion of RSO into biodiesel has been reported in the literature [10, 14]. However, the reported high acid value of RSO renders the conversion into biodiesel difficult [10]. Typically, an acid value of 4 mg KOH/g is set as the maximum for plant oils [15] whereas acid value for RSO between 2 and 81.6 mg KOH/g have been reported [15]. These high free fatty acid (FFA) values are not necessary an intrinsic feature of the RSO, but will be a function of the processing conditions and technology, as well as the storage conditions of the seeds [15].

Literature data on the effect of seed storage on the quality of RSO are scarce and only one study is available [15] (Table 1). In this study, rubber seeds were stored at two different storage conditions viz i) in a controlled laboratory setting (entry 1 in Table 1)

and in a traditional storehouse (entry 2 in Table 1). The acid value of isolated RSO for entry 1 increased from 2 to 8.6 mg KOH/g, whereas a higher difference was found for condition 2 (from 2 to 30.8 mg KOH/g). In the same report, the effect of storage on the acid value of crude RSO was provided [15]. After two months at 27 °C, the acid value increased from 18.1 to 31 mg KOH/g (Table 1, entry 3).

Table 1 Overview of studies on the influence of storage conditions on the acid value of rubber seed, rubber seed oil and rapeseed methyl esters

No	Material	Storage conditions	Acid value (mg KOH/g)		Ref.
			Initial	Final	
1	Rubber seed	Open crates (27 °C, 51 % RH)[a)]	2	8.6 [b)]	[15]
2	Rubber seed	Large storage room (27 °C, 51 % RH)[a]	2	30.8[b)]	[15]
3	RSO	Closed container (27 °C, 51 % RH)[a)]	18.1	31 [b)]	[15]
4	Rapeseed methyl ester	Closed container (4 °C)	0.15	0.22[c)]	[16]
5	Rapeseed methyl ester	Closed container (20 °C)	0.15	0.28[c)]	[16]
6	Rapeseed methyl ester	Closed container (40 °C)	0.15	0.75[c)]	[16]

[a)] estimated room temperature and relative humidity (RH) [b)] after 2 months storage [c)] after 12 months storage

Studies on the influence of storage on relevant product properties of RSO ethyl esters are not available in the open literature. As such, the degradation of rapeseed oil methyl esters under different storage conditions was used as the benchmark [16]. Here, the acid value increased slightly from 0.15 to 0.22 after one year of storage at 4 °C (refer to Table 1 for storage conditions). Higher storage temperatures (from 4 to 40 °C) led to an increase in the acid value from 0.22 to 0.75 mg KOH/g.

Therefore, we can conclude that detailed studies on the effect of storage time of rubber seed on relevant properties are not yet available. In addition, the one step trans-esterification of RSO with ethanol has never been reported before. We here report the influence of storage time on i) the moisture content of rubber seeds and the acid value of the oil within the seeds, ii) the acidity of isolated RSO and iii) the acidity of RSO ethyl esters prepared from RSO. For rubber seeds, the effect of storage conditions on the moisture content of two different rubber seed fraction, one with an initial moisture content of 10.7 wt% and another with a moisture content of 3.1 wt%, were determined and modelled. The latter allowed estimation of the diffusion coefficient of water in the rubber seeds at 27 °C, which has not yet been reported in the literature. In addition, the effect of storage on the acid content of the oil in the rubber seeds, isolated RSO and RSO

ethyl esters was investigated (27 °C, closed vessels). For this purpose, RSO ethyl esters were synthesised and relevant product properties after synthesis were determined, which is an absolute novelty of this paper.

3.2 Materials and Methods

3.2.1 Materials

Seeds from the rubber tree (*Hevea brasiliensis*) were obtained from Bengkulu, Indonesia. The mature fruits were harvested in September 2012. The seeds were dried in open air in the sun for one week before being stored in crates (27 °C). The seeds were stored at room temperature (27 °C) before experiments were carried out at the Institut Teknologi Bandung, Indonesia. The moisture content of the rubber seeds upon receipt was 11 wt%, w.b. (wet based) whereas the moisture content of the dehulled rubber seeds was 8 wt%, w.b. Ethanol (absolute, pro analysis) and n-hexane (99 wt%, for analysis) was obtained from Emsure. Sodium ethoxide solution (21 wt%) in ethanol and $CDCl_3$ (99.8 atom % D) were obtained from Sigma-Aldrich.

3.2.2 Storage conditions

The rubber seeds (20 kg) were split in two fractions of 10 kg. One of the fractions was exposed to a pretreatment (PT) procedure, consisting of drying the seeds in an oven at 60 °C for 3 days (PT). The other fraction was used as such (NPT). Both fractions were stored in a crate (50 cm x 30 cm x 18 cm) at 27 °C, see Table 2 for details. The humidity and temperature of the storage room were measured periodically. In addition, the moisture and oil content of the seeds and the acid value of the isolated RSO samples were periodically monitored for a two months period. RSO and RSO ethyl esters were stored in closed 20 mL glass bottles at 27 °C. The acid values were periodically determined for a two months period. An overview of the storage conditions and measured variables are given in Table 2.

Table 2 Overview of storage conditions for rubber seed, RSO and RSO ethyl ester

Material	Storage conditions	Measured variable
Rubber seeds	No pre-treatment, seeds stored in a crate (50 cm x 30 cm), in layers of 18 cm at 27 °C (NPT)	Humidity, temperature, moisture content, oil content (after Soxhlet extraction), acid value (after isolation)
Rubber seeds	Pre-treatment at (60 °C, 3 days), seeds stored in a crate (50 cm x 30 cm), in layers of 18 cm at 27 °C (PT)	Humidity, temperature, moisture content, oil content (after Soxhlet extraction), acid value (after isolation)
RSO	Stored in a closed container at 27°C	Acid value
RSO ethyl esters	Stored in a closed container at 27°C	Acid value

3.2.3 Determination of the moisture content of the rubber seeds

The total moisture content of the rubber seeds was determined using Method B-1 4 of the German Standard Methods (DGF, 2002). It involves heating the dehulled rubber seeds in the oven at 103 °C until constant weight.

3.2.4 Determination of the oil content of the rubber seeds

The oil contents of the rubber seeds were determined using a Soxhlet extraction, based on method B-1 5 of the German standard methods. The seeds were dehulled and dried overnight at 103 °C before analysis. The dried kernels were grinded using a coffee grinder. Approximately 5 g of sample was weighed with an accuracy of 0.0001 g and transferred to a Soxhlet thimble, covered with cotton wool and extracted with n-hexane for at least 6 h. The solvent was evaporated in a rotary evaporator (atmospheric pressure, 69 °C) and the samples were subsequently dried in an oven at 103 °C until constant weight. The oil content is reported as gram oil per gram sample on a dry basis.

3.2.5 Hydraulic pressing of RSO

A laboratory-scale hydraulic press was used to expel the oil from the rubber seeds. A detailed description of the hydraulic press is described elsewhere [17]. Prior to expression, the seeds were dehulled and dried in an oven at 60 °C for three days. Approximately 7 g of dried kernel (dehulled rubber seeds) was placed in the pressing chamber and pressed at 27 °C and 20 MPa for 10 min. The isolated RSO was stored at 27 °C and the acid value was determined using an acid-base titration.

3.2.6 Synthesis of rubber seed oil ethyl esters

RSO ethyl ester were synthesised in a glass batch reactor (20 mL) immersed in a water bath. The reactor was filled with RSO (5 mL), ethanol (1.2 g, 6:1 molar ratio of ethanol to oil) and sodium ethoxide (0.2 g, 1 wt% catalyst with regards to the oil). The content was stirred using a magnetic stirrer at a rotational speed of 600 rpm. A number of experiments were performed at a range of temperatures (20 to 70 °C). Sampling of the reactor contents was performed at fixed time intervals. The samples were quenched with 0.1 M HCl in water. The top layer was separated and analysed with ^{1}H NMR (Nuclear Magnetic Resonance, *vide infra*).

3.2.7 Product analysis

The biodiesel yield was determined using ^{1}H NMR as described by Abduh et al. [9]. Detailed descriptions of the analytical methods for water content, acid value, flash point, cloud point and pour point are as described elsewhere [9].

The density of the oil was measured at 30-100 °C using a standard picnometer. For this purpose, 10 ml of a sample was placed in the measuring cell and equilibrated to within

0.1 °C of the desired temperature. Reported values are the average of duplicate measurements.

The viscosity of the sample was determined using a cone-and-plate viscometer (AR1000-N from TA instrument) with a cone diameter of 40 mm and a 2° angle. The measurement was performed at 30-100 °C with a shear rate of 15 s^{-1} [18].

3.3 Results and discussion

3.3.1 Rubber seed characteristics

The experiments were carried out with fresh rubber seeds obtained from Bengkulu, Indonesia. The seeds contain 61 wt%, d.b. (dry basis) kernels, and the remainder being the shells. The initial moisture content of the seeds and kernels as received were approximately 11 and 8 wt%, w.b. (wet basis), respectively. The dehulled seeds had an average oil content of 49.7 wt% d.b., as determined by a Soxhlet extraction with n-hexane. This value is within the 40-50 wt% oil content range as reported in the literature [10].

3.3.2 Effect of storage time of the moisture content of the rubber seeds

The effect of the storage time on the moisture content of the rubber seeds was determined for rubber seeds with two initial moisture contents (3 wt%, and 10.8 wt%). For the latter, the seeds as received were used (NPT), whereas the seeds with the reduced moisture content were obtained by drying the seeds for 3 days at 60 °C (PT). The temperature and relative humidity (RH) of the storage room were measured periodically for a 60 day period (Fig. 1) and was shown to be about constant (27°C, 67% RH). Samples of both seed fractions (NPT, PT) were also taken periodically and the moisture content was determined, see Fig. 2 for details.

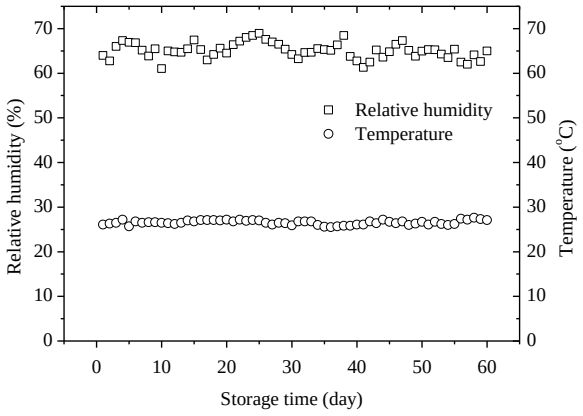

Figure 1. Temperature and relative humidity of the rubber seed storage room

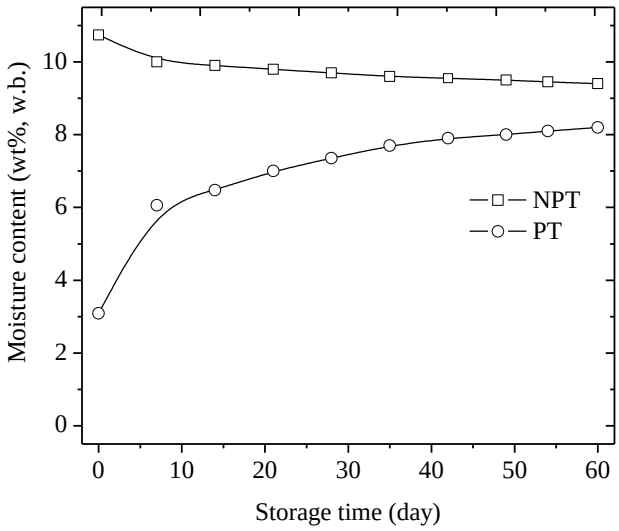

Figure 2. Effect of storage time on moisture content of the rubber seeds (27 °C, 65 % RH)

The moisture content of the pre-dried seeds increased slowly in time and after 60 days, equilibrium was not yet attained. Similarly, the moisture content of the non-treated, as received, reduces slowly. Extrapolation suggest that the equilibrium moisture value of the rubber seeds at the prevailing storage conditions is about 9 wt%. This value is in the range reported for jatropha, soybean, sunflower and linseed as shown in Table 3.

Table 3 Equilibrium moisture values for different oilseeds

Oilseed	Equilibrium moisture content (wt%)	Storage temperature (°C)	RH (%)	Ref.
Jatropha	8.6	25-30	60-70	[17]
Soybean	10.1	25	65	[19]
Sunflower	7.4	25	65	[19]
Linseed	8	25	65	[19]

3.3.3 Modelling of the moisture content of the rubber seeds versus time

The rubber seed moisture content versus time profiles (Fig. 2) were modelled using an analytical solution of the diffusion equation for a sphere, see eq 1 for details [20-22].

$$MR = \frac{M-M_0}{M_e-M_0} = 1 - \frac{6}{\pi^2}\sum_{m=1}^{\infty}\frac{1}{m^2}e^{\left[\frac{-m^2\pi^2 D_{eff}t}{r_0^2}\right]} \quad (1)$$

Where

MR	Moisture ratio at time t (wt%)
M	Moisture content at time t (wt%)
M_0	Initial moisture content (wt%)
M_e	Equilibrium moisture content (wt%)
D_{eff}	Effective diffusion coefficient (m^2/s)
r_0	Radius (m)
t	Time (s)
m	Counter

The following assumptions were made:

1. The initial concentration of water is uniform throughout the kernel
2. For time > 0, the surface and the moisture concentration of the environment are in equilibrium and surface resistance is negligible
3. The moisture content of the environment is constant
4. The diffusion coefficient of water in the kernel is independent of the moisture concentration
5. The rubber seeds are spherical with an average radius of 0.015 m.

The experimental data as given in Fig. 2 for both rubber seed fractions were modelled using eq. (1), and this allowed the determination of the equilibrium moisture content of the seeds (at 67% RH and 27 °C) and the diffusion coefficients of water in the rubber seeds. The results are shown in Table 4 and Fig. 3. The model is in good agreement with the experimental data.

Table 4 Estimated equilibrium moisture content of rubber seeds and effective diffusion coefficient of water in the rubber seeds[a)]

Parameter	NPT	PT
M_e (wt%)	9.02 ± 0.09	8.97 ± 0.08
D_{eff} (m^2/s)	$0.49 \times 10^{-11} \pm 0.06 \times 10^{-11}$	$10^{-11} \pm 0.09 \times 10^{-11}$

[a)]obtained by solving eq. (1), 27°C, 67% RH

The estimated equilibrium moisture content of both rubber seed fractions is identical within the experimental error and approximately 9.0 wt%, in line with other oil seeds (Table 3). The modelled diffusion coefficient of water in the rubber seeds as received (NPT) is 0.49×10^{-11} m^2/s, which is slightly lower than for the pre-dried samples (PT, 0.78×10^{-11} m^2/s). These differences are likely due to the occurrence of structural changes upon drying after 3 days for 60 h (PT). To the best of our knowledge, the moisture diffusion coefficient of water in rubber seeds has not yet been reported to

date. The modelled diffusion coefficients for NPT and PT are slightly higher than the diffusion coefficients of water in wheat viz. 0.22-0.31 x 10^{-11} m^2/s (27-31 °C) [23].

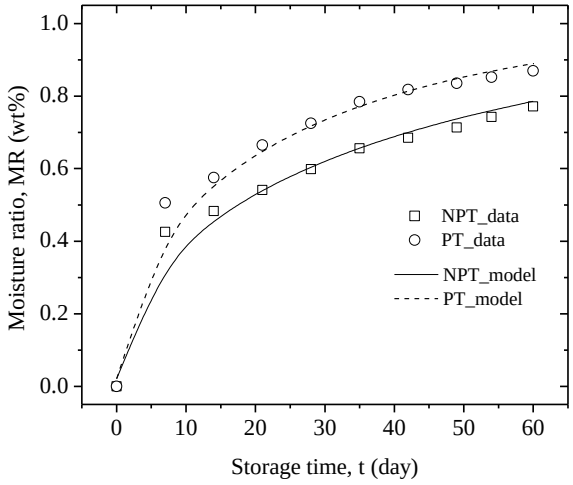

Figure 3. Moisture ratio as a function of time for both rubber seed fractions

3.3.4 Oil content of rubber seeds and acid value versus storage time

The oil content of the kernel (dehulled rubber seeds) for both seed fractions (NPT and PT) was determined periodically by taking a certain amounts of seeds and subjecting them to a standardized Soxhlet extraction with n-hexane. The initial oil content of the rubber seeds as received was 49.7 wt%, d.b. After two months of storage, the oil content was slightly reduced to 47.8 wt%, d.b. Similar observations were found for the oil content of the pre-dried rubber seeds (48.9 wt%, d.b. after 2 months versus 49.7 wt%, d.b. initial oil content). As such, the oil content is not largely affected by the time of storage, at least not for a period of two months.

However, the acid value of the RSO obtained after pressing the seeds increased from 0.8 to 4.2 mg KOH/g for NPT and 0.5 to 2.1 mg KOH/g for PT upon storage, as shown in Fig. 4. Thus, it can be concluded that the acid value of the RSO in the stored seeds is a function of the storage time, with longer times leading to higher acid values. In addition, the effect is more pronounced for seeds with a higher initial water content (NPT). As such, a thermal pre-treatment to reduce the moisture content of seeds before storage may have a positive effect on the acid value development versus time of the isolated RSO.

These findings suggest that water plays a role in the development of acid components in the seeds. This may be rationalised by considering that the acid species formed upon

storage are likely free fatty acids, formed by the hydrolysis of triglycerides, possibly catalysed by enzymes present in the seeds. As such, a higher water content in the seeds is expected to favor FFA formation. In addition, the rate of FFA formation in the dried seeds may also be reduced due to a (partly) deactivation of the enzymes by the pre-treatment at 60 °C for 3 days. The range of acid values of the RSO for the storage experiments is relatively low (0.5- 4.2 mg/kg KOH) compared to the acid value reported in the literature for RSO, which varies from 2 to 81.6 mg KOH/g [15].

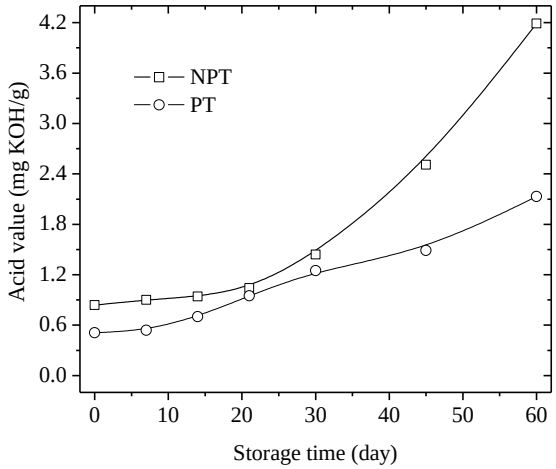

Figure 4. Effect of storage time on acid value of pressed RSO for NPT and PT

3.3.5 Influence of storage time on the acid value of RSO

Besides detailed knowledge on the effect of storage time on relevant properties of the rubber seeds (*vide supra*), it is also of high relevance to get insights in the effect of storage time on the product properties of the RSO. For this purpose, a freshly prepared sample of RSO was prepared. Seeds as received were dehulled and dried in an oven at 60 °C for three days. The kernels were pressed using a laboratory scale hydraulic press (20 MPa, 35 °C, 10 min). Relevant properties of the RSO were determined and are shown in Table 5. The water content, flash point, pour point and cloud point resembles other plant oils reported in the literature [1].

The isolated and characterised RSO was stored at 27 °C in a closed container and the acidity, a very important product quality indicator, was periodically measured using an acid-base titration. The results are shown in Fig. 5. The initial acid value was 0.52 mg KOH/g, and slightly increased to 0.6 mg KOH/g upon storage. The trend is different from the acid development curve observed for the rubber seeds, where the acidity increase in time is much more pronounced than for the oil. A likely explanation is the

by far lower water content in the oil (300 ppm) than in the seeds, which will affect the rate of hydrolysis of triglycerides. In addition, enzyme activity is likely negligible in the pressed oil. [15]. Zhu et al. observed that the acid value of a crude RSO increased from 18.1 to 31 mg KOH/g after 2 months of storage, an increase of 71 % as compared to only 15% observed in this study. A possible explanation for the differences is differences in initial water content of the samples.

Table 5 Properties of isolated RSO[a)]

Property	RSO
Density at 40 °C (kg/m^3)	920
Viscosity at 40 °C (Pa.s)	0.033
Acid Value (mg KOH/g)	0.52
Water Content (mg/kg)	300
sh point (°C)	)
ır point (°C)	
ud point (°C)	

[a)] pressing conditions: 20 MPa, 35 °C, dried kernels (negligible moisture content)

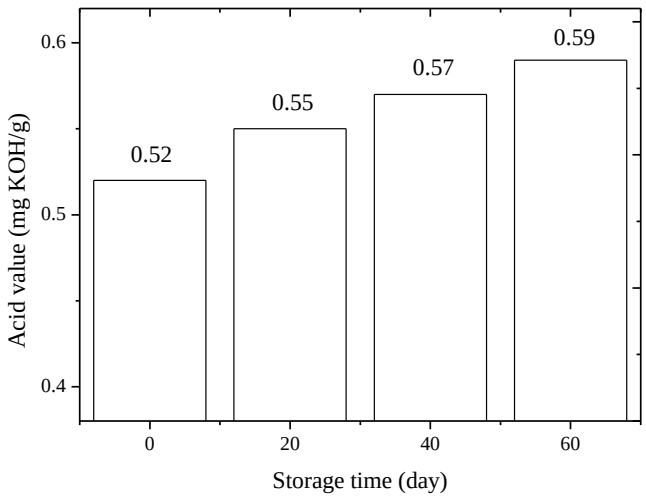

Figure 5. Effect of storage time on acid value of stored rubber seed oil

3.3.6 Influence of storage time on the acid value of RSO ethyl esters

3.3.6.1 Synthesis of RSO ethyl esters

The isolated RSO obtained in the previous section was used as a feed for the synthesis of RSO ethyl esters (RSOEE). The esters were prepared by the reaction of the RSO with ethanol using sodium ethoxide as the catalyst in a batch set-up. The low acid value of

the RSO (0.6 mg KOH/g) eliminates the necessity of a two step esterification reaction (initially an acid catalysed reaction followed by a base catalysed reaction) as proposed in another study [10]. The ethanolysis of RSO was performed at the conditions similar to the ethanolysis of jatropha oil, which was reported previously by our group [9]. The catalyst concentration, ethanol to oil ratio and rotational speed was set at the optimum conditions as determined in our previous study for jatropha oil (1 wt% with respect to the oil, 6:1 molar ratio of ethanol to oil, 600 rpm). During reaction, samples were taken for analyses, allowing preparation of conversion versus time profiles. A number of experiments were carried out within a range of temperature (20-70 °C) and the results are presented in Fig. 6.

As expected, higher reaction temperatures not only enhance the rate of the esterification reaction but also lead to higher biodiesel yields (Fig. 6). For instance, the ester yield was 98 mol% at 70 °C compared to 88 mol% at 20 °C. This observation is in line with previous findings in our group that the maximum (equilibrium) conversion for the synthesis of fatty acid ethyl ester (FAEE) from jatropha oil increased from 93 mol% at 50 °C to 98 mol% at 70 °C. This indicates that the equilibrium position of the trans-esterification reactions shifts to the right at higher temperatures, implying that the trans-esterification reaction is slightly endothermic.

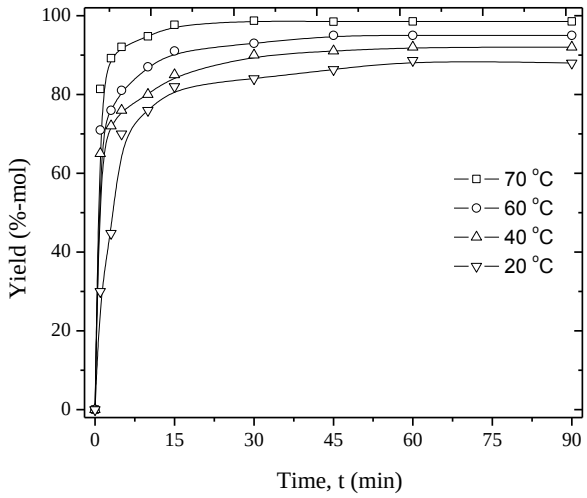

Figure 6. Biodiesel yield versus time for the ethanolysis of RSO in a batch set-up (6:1 molar ratio of ethanol to oil, 1 wt% of catalyst concentration with respect to the oil, 600 rpm)

The esters yields are higher than reported for the trans-esterification of RSO using methanol and NaOH as the catalyst (85%, 6:1 molar ratio of methanol to oil, 1 wt%

catalyst with respect to the oil, 30 °C) [14]. This implies that the ethanolysis of RSO is faster than methanolysis, supported by other studies [24, 25]. However, literature data are conflicting and others report that the reaction with methanol is faster than with ethanol [26-28]. These contradictory results are likely due to the fact that the reaction is a reactive liquid-liquid system, for which the overall kinetics are not only determined by intrinsic kinetics of the reaction but also by mass transport of reactive components between the liquid-liquid (L-L) interface. As such, differences in stirring speed, the type of impeller (simply a magnetic stirring bar or a well-designed impeller) and geometry of the reactor may play an important role. Regarding mass transfer limitations, these are expected to be less important in ethanol as the solubility of the plant oil in ethanol is better than in methanol [25].

3.3.6.2 Relevant product properties of RSOEE

Relevant properties of the freshly synthesised RSOEE (6:1 molar ratio of ethanol to oil, 1 wt% of catalyst concentration with respect to the oil, 600 rpm, 70 ^{o}C) were determined and are provided in Table 6. When possible, the properties were compared to the biodiesel standard of EN 14214 for methyl esters. The acid value, water content, sodium content, phosphorus content, and flash point are all within specifications.

Table 6 Properties of RSOEE

Property	ROSEE	EN 14214
Acid Value (mg KOH/g)	0.32	0.5 mg KOH/g max
Water Content (mg/kg)	400	500 mg/kg max
Na content (mg/kg)	4	5 mg/kg max
P content (mg/kg)	2	10 mg/kg max
Flash point (°C)	171	120 ^{o}C min
Pour point (°C)	-2	-
Cloud point (°C)	0	-

The RSOEE was stored in a closed container at 27 °C and the acid value was monitored in time (60 days) using an acid-base titration. The acid value upon storage is about constant; from 0.32 to 0.33 mg KOH/g after 2 months. This is in agreement with the work by Leung et al. that storage of biodiesel in a closed container at room temperature is less susceptible to degradation compared to exposure to air and storage at 40 °C [16].

3.3.7 Comparison of the acid value versus time profiles for rubber seeds, RSO and RSOEE

The initial and final acid values after storage (2 month, 27°C) for the oil in the rubber seeds, isolated RSO and RSOEE are shown in Table 7 and compared with literature data. The relative increase of the acid value for the oil in the rubber seeds upon storage is about the same for the two rubber seed samples used in this study (NPT, PT, 320-330%). This result is in line with the data reported by Zhu et al. for rubber seeds after

2 month of storage in open crates at 27°C and 51% RH (Table 1, entry 1). Worse results were reported by Zhu for rubber seeds stored in piles, which showed a 1400% relative increase in acid content upon storage at 27 °C (Table 1, entry 2). This is likely due to poor ventilation leading to a higher pile temperature and Mildew infection which caused an increase in the acid value [15].

The relative increase in the acidity of the isolated RSO and RSOEE after storage is less than for the oil in the seeds. This result indicates that it is advantageous to store the isolated oil instead of the seeds to avoid excessive built up of acids, rendering the product off- specification.

Table 7 Acid values for rubber seeds, RSO and RSOEE

Material	Acid value (mg KOH/g)		Relative increase
	Initial	Final	(%)
Rubber seed			
- NPT[a)]	0.8	4.2	425
- PT[a)]	0.5	2.1	320
- Entry 1 (Table 1)[b)]	2	8.6	330
- Entry 2 (Table 1)[b)]	2	30.8	1440
Oil			
- RSO [a)]	0.52	0.6	15
- RSO [b)]	18.1	31	71
Biodiesel			
- RSO ethyl ester [a)]	0.32	0.33	3
- Rapeseed methyl ester [c)]	0.15	0.22	47

[a)] this study, after 2 months storage [b)] Zhu et al. after 2 months storage [15] [b)] Leung et al., after 12 months storage [16]

3.4 Conclusions and outlook

The influence of rubber seed storage time on the quality of rubber seed oil has been investigated. Long-term seed storage increased the acid value of the oils in the rubber seeds. A seed pre-treatment procedure (drying at 60°C for 3 days) was shown to have a positive effect and the extent of acid value development in time was lower than for the non-pretreated fraction. In addition, the effect of storage time on the product quality and particularly the acid value of isolated rubber seed oil and rubber seed ethyl esters has also been evaluated. Freshly isolated rubber seed oil and rubber seed ethyl esters were shown to have a low acid value of 0.52 and 0.32 mg KOH/g, respectively. The acid values only slightly increased upon storage in closed containers (2 month, 27°C). As such, it is recommended to store the isolated RSO instead of storing the rubber seeds to minimise acid formation in the rubber oil. Formation of the latter should be avoided as acids are known to cause major issues during subsequent use (e.g. in stationary engines) and processing (e.g. for biodiesel synthesis) of plant oils.

3.5 References

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